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[Title of the Invention] TONER AND IMAGE-FORMING APPARATUS
USING THE TONER

[Claims]

[Claim 1] A toner comprising toner mother particles containing a binding resin and a colorant having added thereto external additives, wherein the external additives are added by multistage process, and particles comprising at least a long chain fatty acid or a salt of it are added in the final stage of the multistage process.

[Claim 2] The toner as claimed in claim 1, wherein at least one external additive selected from the group consisting of negatively electrifiable silica fine particles, titanium oxide and positively electrifiable silica fine particles is added to the toner mother particles, and particles comprising at least a long chain fatty acid or a salt of it are added to the toner mother particles in the last place.

[Claim 3] The toner as claimed in claim 1 or 2, wherein negatively electrifiable silica fine particles are added to the toner mother particles in the first place in the multistage process.

[Claim 4] The toner as claimed in claim 3, wherein the multistage process is process performing in the order of: a process of adding negatively electrifiable silica

fine particles to the toner mother particles; a process of adding titanium oxide fine particles; a process of adding positively electrifiable silica fine particles; and a process of adding particles comprising a long chain fatty acid or a salt of it.

[Claim 5] The toner as claimed in claim 3, wherein the multistage process is process performing in the order of: a process of adding negatively electrifiable silica fine particles to the toner mother particles; a process of adding titanium oxide fine particles; and a process of adding positively electrifiable silica fine particles and particles comprising a long chain fatty acid or a salt of it.

[Claim 6] The toner as claimed in claim 3, wherein the multistage process is process containing: a process of adding negatively electrifiable silica fine particles to the toner mother particles; a process of adding titanium oxide fine particles; and a process of adding particles comprising a long chain fatty acid or a salt of it.

[Claim 7] The toner as claimed in claim 3, wherein the multistage process is process performing in the order of: a process of adding negatively electrifiable silica fine particles to the toner mother particles; and a process of adding titanium oxide fine particles, positively electrifiable silica fine particles and particles

comprising a long chain fatty acid or a salt of it at the same time.

[Claim 8] The toner as claimed in claim 1 or 2, wherein negatively electrifiable silica fine particles and titanium oxide fine particles are added to the toner mother particles in the first place.

[Claim 9] The toner as claimed in claim 1 or 2, wherein titanium oxide fine particles are added to the toner mother particles in the first place.

[Claim 10] The toner as claimed in claim 1 or 2, wherein the toner mother particles are negatively electrified.

[Claim 11] The toner as claimed in claim 10, wherein the toner mother particles have a quantity of electrification of from -5 to -60 $\mu\text{C/g}$.

[Claim 12] The toner as claimed in claim 10 or 11, wherein the multistage process is process performing in the order of: a process of adding at least positively electrifiable silica fine particles to the negatively electrified toner mother particles in the first place; and a process of adding at least particles comprising a long chain fatty acid or a salt of it in the last place.

[Claim 13] The toner as claimed in claim 12, wherein negatively electrifiable silica fine particles are added before particles comprising a long chain fatty acid

or a salt of it are added.

[Claim 14] The toner as claimed in claim 12, wherein the multistage process is process performing in the order of: a process of adding positively electrifiable silica fine particles to the negatively electrified toner mother particles; and a process of adding titanium oxide fine particles and particles comprising a long chain fatty acid or a salt of it at the same time.

[Claim 15] The toner as claimed in claim 12, wherein the multistage process is process performing in the order of: a process of adding positively electrifiable silica fine particles to the negatively electrified toner mother particles; a process of adding titanium oxide fine particles; and a process of adding particles comprising a long chain fatty acid or a salt of it.

[Claim 16] An image-forming apparatus which is stocked with the toner as claimed in any of claims 1 to 15.

[Claim 17] The image-forming apparatus as claimed in claim 16, which is at least equipped with a latent image carrier on which an electrostatic latent image is formed; a toner carrier for carrying a toner to the latent image carrier for developing the electrostatic latent image on the latent image carrier; and a developing chamber having a toner regulating member to regulate the amount of the toner carried to the latent image carrier by the toner carrier.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a toner which is used for developing an electrostatic latent image in electrophotography, electrostatic recording and electrostatic printing and for forming an image by thermal fixation, and also relates to an image-forming apparatus using the toner.

[0002]

[Background Art]

The toner for forming electrostatic images generally comprises, as the toner mother particles, fine particles of a binding resin containing a coloring component, e.g., a dye or a pigment, and, if necessary, an electrification controlling agent, and the toner is manufactured by a method of adding external additives to the outside (surface) of the toner mother particles for the purpose of providing flowability or controlling an electrification property. As the external additives, positively electrifiable silica fine particles, negatively electrifiable silica fine particles, inorganic fine particles other than silica (e.g., titanium oxide), fatty acid metal salt and the like are used.

[0003]

In general, the toner for forming electrostatic images is negatively electrified. Such a toner is manufactured by the method of preparing negatively electrifiable toner mother particles and adding external additives, e.g., positively electrifiable silica fine particles, etc., to the negatively electrifiable toner mother particles, to thereby control the quantity of negative electrification (refer to, e.g., patent literature 1 to 3). Alternatively, when from weakly negatively electrifiable toner mother particles to positively electrifiable toner mother particles are used, there is a method of adding external additives, such as negatively electrifiable silica fine particles, etc., to the above toner mother particles to control the quantity of negative electrification (refer to, e.g., patent literature 4 to 6).

[0004]

As the methods of manufacturing a toner by using negatively electrifiable toner mother particles, a method of externally adding positively electrifiable hydrophobic silica fine particles to toner mother particles comprising a negatively electrifiable binding resin,, a method of externally adding positively electrifiable hydrophobic silica fine particles and negatively electrifiable hydrophobic silica fine particles (refer to, e.g., patent literature 1 and 2), and a method of externally adding

positively electrifiable hydrophobic silica fine particles and inorganic fine particles having a low electrical resistance value (refer to, e.g., patent literature 3) are exemplified.

[0005]

On the other hand, when weakly negatively electrifiable to positively electrifiable toner mother particles are used in manufacturing a toner, external addition methods are also examined. For example, a method of externally adding positively electrifiable hydrophobic silica fine particles and negatively electrifiable hydrophobic silica fine particles at the same time (refer to, e.g., patent literature 4), and a method of externally adding a first component, a second component, a third component and a fourth component to toner mother particles at the same time, or externally adding the first component lastly, taking hydrophobic silica fine particles or hydrophobic titania as the first component, hydrophobic silica fine particles or hydrophobic titania having larger particle sizes than the particle sizes of component 1 as the second component, inorganic fine particles as the third component, and a fatty acid metal salt as the fourth component (refer to, e.g., patent literature 5) are known.

[0006]

Further, there is disclosed in a patent literature a

method to obtain a toner in which the liberation of external additives is restrained by externally adding in the order of titanium oxide fine particles and silica fine particles to toner mother particles (refer to, e.g., patent literature 6).

[0007]

However, in the toners obtained by the methods disclosed in patent literature 1 to 6, external additives (positively electrifiable silica fine particles, negatively electrifiable silica fine particles, titanium oxide fine particles and the like), which function to control electrification or flowability, are liable to be desorbed from the surface of the toner, which causes the reduction of flowability or electrification property of the toners, as a result, transfer efficiency and image density are depressed.

[0008]

In addition, it is disclosed in patent literature 1 and 5 to use the metal salt of a fatty acid (a metal soap) in the toner for electrophotography, and the cases of using the metal salt of a fatty acid besides the above are also disclosed in patent literature 7 to 12. In patent literature 5, a fatty acid metal salt is used in view of the prevention of fixing of a toner and generation of black spots on the surface of a photosensitive material, and then

hydrophobic silica or hydrophobic titania is added.

However, there is a problem that the external additive hydrophobic silica or hydrophobic titania is liberated, so that the stability of electrification cannot be maintained for a long period of time.

[0009]

Patent literature 7 perceived the binding property of a fatty acid metal salt and obtained a toner by the external addition process of only one time of the addition of a fatty acid metal salt with silica having amino groups on the surface at the same time. Although the toner obtained by this method is improved a little in the point of the rate of liberation of hydrophobic silica, a problem that the quantity of electrification of the toner cannot be maintained stably is still left behind. Patent literatures 8 to 12 also disclose the use of fatty acid metal salts as the external additive in manufacturing toners. However, in any of the above patent literature similarly to patent literature 7, the fatty acid metal salts are added simultaneously with other external additives to obtain toners by the external addition process of only one time. The toners disclosed in patent literatures 7 to 12 also have problems that the quantity of electrification of the toners cannot be maintained stably.

[0010]

[Patent literature 1]

JP-A-2000-267337 (the term "JP-A" as used herein means an "unexamined published Japanese patent application").

[Patent literature 2]

JP-A-2002-14487

[Patent literature 3]

JP-A-2002-214834

[Patent literature 4]

JP-A-11-231571

[Patent literature 5]

JP-A-2001-100452

[Patent literature 6]

JP-A-2002-72544

[Patent literature 7]

Japanese Patent No. 2502353

[Patent literature 8]

JP-B-8-33681 (the term "JP-B" as used herein means an "examined Japanese patent publication").

[Patent literature 9]

Japanese Patent No. 2759510

[Patent literature 10]

JP-A-9-114129

[Patent literature 11]

JP-A-11-323396

[Patent literature 12]

JP-A-2001-296688

[Patent literature 13]

JP-A-2002-202622

[0011]

[Problems to be Resolved by the Invention]

An object of the present invention is to provide a toner which is low in desorption of external additives (e.g., positively electrifiable silica fine particles, negatively electrifiable silica fine particles, titanium oxide fine particles and the like), can maintain the electrification property for a long period of time, shows high flowability and transfer efficiency, and is not accompanied by the reduction of image density.

[0012]

[Means of Solving the Problems]

The present invention provides a toner comprising toner mother particles containing a binding resin and a colorant having added therewith external additives, wherein the external additives are added by multistage process, and particles comprising at least a long chain fatty acid or a salt of it are added in the final stage of the multistage process.

[0013]

In a preferred embodiment of the present invention,

the toner of the invention is manufactured by adding at least one external additive selected from the group consisting of negatively electrifiable silica fine particles (silica fine particles having a negative electrification property), titanium oxide and positively electrifiable silica fine particles (silica fine particles having a positive electrification property) to the toner mother particles, and adding in the last place particles comprising at least a long chain fatty acid or a salt of it to the toner mother particles.

[0014]

In a more preferred embodiment of the invention, negatively electrifiable silica fine particles are added to the toner mother particles in the first place in the multistage process.

[0015]

In another preferred embodiment, the multistage process is process performing in the order of a process of adding negatively electrifiable silica fine particles to the toner mother particles; a process of adding titanium oxide fine particles; a process of adding positively electrifiable silica fine particles; and a process of adding particles comprising a long chain fatty acid or a salt thereof.

[0016]

In a further preferred embodiment, the multistage process is process performing in the order of a process of adding negatively electrifiable silica fine particles to the toner mother particles; a process of adding titanium oxide fine particles; and a process of adding positively electrifiable silica fine particles and particles comprising a long chain fatty acid or a salt thereof.

[0017]

In a still further preferred embodiment, the multistage process is process containing a process of adding negatively electrifiable silica fine particles to the toner mother particles; a process of adding titanium oxide fine particles; and a process of adding particles comprising a long chain fatty acid or a salt thereof.

[0018]

In another embodiment, the multistage process is process performing in the order of a process of adding negatively electrifiable silica fine particles to the toner mother particles; and a process of adding titanium oxide fine particles, positively electrifiable silica fine particles and particles comprising a long chain fatty acid or a salt thereof at the same time.

[0019]

In another embodiment, negatively electrifiable silica fine particles and titanium oxide fine particles are

added to the toner mother particles in the first place.

[0020]

In a preferred embodiment, titanium oxide fine particles are added to the toner mother particles in the first place.

[0021]

In another preferred embodiment, the toner mother particles are negatively electrified, and the toner mother particles have a quantity of electrification of from -5 to -60 $\mu\text{C/g}$.

[0022]

In another more preferred embodiment, the multistage process is process performing in the order of a process of adding at least positively electrifiable silica fine particles to the negatively electrified toner mother particles in the first place; and a process of adding at least particles comprising a long chain fatty acid or a salt thereof in the last place.

[0023]

In another further preferred embodiment, negatively electrifiable silica fine particles are added before particles comprising a long chain fatty acid or a salt thereof are added.

[0024]

In another still further preferred embodiment, the

multistage process is process performing in the order of a process of adding positively electrifiable silica fine particles to the negatively electrified toner mother particles; and a process of adding titanium oxide fine particles and particles comprising a long chain fatty acid or a salt thereof at the same time.

[0025]

In a preferred embodiment, the multistage process is process performing in the order of a process of adding positively electrifiable silica fine particles to the negatively electrified toner mother particles; a process of adding titanium oxide fine particles; and a process of adding particles comprising a long chain fatty acid or a salt thereof.

[0026]

The present invention further provides an image-forming apparatus which is stocked with any of the above-described toners. A preferred image-forming apparatus is at least equipped with a latent image carrier on which an electrostatic latent image is formed; a toner carrier for carrying a toner to the latent image carrier for developing the electrostatic latent image on the latent image carrier; and a developing chamber having a toner regulating member to regulate the amount of the toner carried to the latent image carrier by the toner carrier.

[0027]

[Detailed Description of the Preferred Embodiment]

The toner in the present invention is a toner obtained by the addition of external additives, the external additives are added by multistage process, and the toner is obtained by adding the external additives containing particles comprising at least a long chain fatty acid or a salt of it to toner mother particles in the final stage of the multistage process. In the toner obtained by adding particles comprising at least a long chain fatty acid or a salt thereof in the last place, the liberation of the externally added external additives is inhibited by the long chain fatty acid or the salt thereof, thereby the quantity of electrification of the toner can be maintained stably for a long period of time and also excellent in flowability. Further, by adding a long chain fatty acid or a salt thereof in the final stage of the toner manufacturing process and making the long chain fatty acid or the salt thereof present at the outermost shell of the toner mother particles, the adhesion of the toner with the photosensitive material or of the toner with the intermediary belt in the developing chamber is reduced, thereby the transfer efficiency in the transfer process can be improved, and the abrasion of the photosensitive material and the intermediary belt by the external

additives on the surface of the toner can also be prevented.

[0028]

In the specification of the invention, materials externally added to toner mother particles, e.g., negatively electrifiable silica fine particles, positively electrifiable silica fine particles, titanium oxide fine particles, and particles comprising a long chain fatty acid or a salt thereof are referred to as external additives, and adding these external additives to the exteriors (surfaces) of toner mother particles is called external addition.

[0029]

The materials which are used in the invention, e.g., (i) toner mother particles and the materials constituting the toner mother particles (so-called internal additives, e.g., binding resins, colorants, mold releasing agents, dispersants, electrification controlling agents, and magnetic agents), (ii) negatively electrifiable silica fine particles, (iii) positively electrifiable silica fine particles, (iv) titanium oxide fine particles, (v) long chain fatty acids or salts thereof, and (vi) inorganic fine particles which are added according to necessity, are described in the first place, and then the toner of the present invention is described.

[0030]

(I) Materials which are used in the present invention:

(i) Toner mother particles:

Toner mother particles contain a binding resin and a colorant and, if necessary, internal additives, e.g., a mold releasing agent, a dispersant, an electrification controlling agent, and a magnetic agent. Toner mother particles are positively or negatively electrified, preferably negatively electrified. There are some methods to electrify toner mother particles so as to have an appropriate range of the quantity of negative electrification. For example, a method of blending a negative electrification controlling agent with a positively electrifiable binding resin, a method of further blending a negative electrification controlling agent when the electrification property of a negatively electrifiable resin is not sufficient, or a method of making a binding resin itself negatively electrifiable resin. The materials which constitute toner mother particles and the manufacturing method of toner mother particles are described in order below.

[0031]

(i-1) Materials constituting toner mother particles:

(Binding resins)

Considering the methods of electrifying toner mother particles negatively, any of positively electrifiable

resins and negatively electrifiable resins can be used as binding resins. As such resins, resins which are ordinarily used as the materials of toners are used. For example, polystyrene-based resins, acrylate-based resins or methacrylate-based resins (hereinafter referred to as (meth)acrylate-based resins), styrene-acrylic-based resins, polyester resins, polyethylene resins, epoxy resins, silicone resins, polypropylene resins, fluorine resins, polyamide resins, polyvinyl alcohol resins, polyurethane resins, polyvinyl butyral resins, and copolymers containing the constituents of these resins are used.

[0032]

Of these resins, as positively electrifiable to weakly negatively electrifiable resins, polystyrene-based resins and styrene-(meth)acrylate-based resin copolymers are preferably used. As weakly negatively electrifiable to strongly negatively electrifiable resins, polyester resins are preferably used.

[0033]

As polystyrene resins, e.g., hydrogenated styrene resins, styrene-isobutylene copolymers, acrylonitrile-butadiene-styrene copolymers (ABS resins), acrylonitrile-styrene copolymers (AS resins), acrylonitrile-polyethylene chloride-styrene copolymers (ACS resins), styrene-p-chlorostyrene copolymers, styrene-propylene copolymers,

styrene-butadiene crosslinked polymers, styrene-butadiene-chlorinated paraffin copolymers, styrene-allyl alcohol copolymers, styrene-butadiene rubbers, styrene-maleic ester copolymers, styrene-isobutylene copolymers, and styrene-maleic anhydride copolymers are exemplified.

[0034]

As styrene-(meth)acrylate-based resin copolymers, e.g., acrylate-styrene-acrylonitrile copolymers (ASA resins), styrene-diethylaminoethyl methacrylate copolymers, styrene-methyl methacrylate copolymers, styrene-n-butyl methacrylate copolymers, styrene-methyl methacrylate-n-butyl acrylate copolymers, styrene-methyl methacrylate-butyl allylate-N-(ethoxymethyl)acrylamide copolymers, styrene-glycidyl methacrylate copolymers, styrene-butadiene-dimethylaminoethyl methacrylate copolymers, styrene-acrylate-maleate copolymers, styrene-methyl methacrylate-2-ethylhexyl acrylate copolymers, styrene-n-butyl allylate-ethyl glycol methacrylate copolymers, styrene-n-butyl methacrylate-acrylic acid copolymers, styrene-n-butyl methacrylate-maleic anhydride copolymers, styrene-butyl acrylate-isobutylmaleic half ester-divinylbenzene copolymers, styrene-butadiene-acrylate copolymers, and styrene-acrylate copolymers are exemplified.

[0035]

In general, negative electrification controlling

agents are added to these binding resins, thereby toner mother particles having an appropriate quantity of negative electrification are manufactured.

[0036]

These negatively electrifiable resins are relatively preferably used in manufacturing toner mother particles. In particular, when a strongly negatively electrifiable resin is used, it becomes possible to obtain good electrification characteristics without externally adding negatively electrifiable silica fine particles to toner mother particles, and the fixing temperature of the toner can be set at a low temperature.

[0037]

As generally used negatively electrifiable resins, resins having a substituent, e.g., a carboxyl group, a phenyl group, a thiophenyl group or a sulfonic acid group, on the side chain are preferably used. It is preferred that these substituents take the form of a metal salt. As the metal salt, a metal salt with zinc, magnesium, aluminum, sodium, potassium, chromium, iron, manganese or cobalt is preferred. Alternatively, these substituents may be in the form of a salt with an organic base, e.g., an ammonium ion, a pyridinium ion or an imidazolium ion.

[0038]

As the negatively electrifiable resins, polyester

resins are most preferably used. Such polyester resins have a carboxyl group on the side chain which can be obtained by polycondensation of polyhydric alcohols with polyvalent carboxylic acids or derivatives thereof.

[0039]

As the polyhydric alcohols which constitute polyester resins, dihydric alcohols, trihydric alcohols or tetrahydric or higher alcohols are used.

[0040]

The examples of dihydric alcohols include ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, dipropylene glycol, ethylene oxide adducts of bisphenol A and propylene oxide adducts of bisphenol A.

[0041]

The examples of trihydric alcohols include glycerol, trimethylolpropane, trimethylolethane, 1,2,4-butanetriol, 1,2,5-pentanetriol, 2-methylpropanetriol, 2-methyl-1,2,4-butanetriol, and 1,3,5-trihydroxymethylbenzene.

[0042]

The examples of tetrahydric or higher alcohols include sorbitol, 1,2,3,6-hexanetetraol, 1,4-sorbitan, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0043]

These polyhydric alcohols are used alone or as mixtures. Of these polyhydric alcohols, neopentyl glycol, trimethylolpropane, ethylene oxide adducts of bisphenol A and propylene oxide adducts of bisphenol A are preferably used.

[0044]

As the polyvalent carboxylic acids which constitute the polyester resins, divalent carboxylic acids, trivalent or higher carboxylic acids and derivatives of these carboxylic acids are exemplified.

[0045]

The examples of divalent carboxylic acids include malonic acid, succinic acid, glutaric acid, adipic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, phthalic acid, terephthalic acid and isophthalic acid. As the derivatives of divalent carboxylic acids, lower alkyl esters and acid anhydrides of these acids are used. As the lower alkyl esters, alkyl esters having from 1 to 12 carbon atoms, e.g., methyl esters and ethyl esters are preferably used.

[0046]

Of these divalent carboxylic acids, divalent carboxylic acids having an aromatic ring, e.g., phthalic acid, terephthalic acid, isophthalic acid, lower alkyl esters and acid anhydrides of these acids are preferably

used.

[0047]

The examples of trivalent or higher carboxylic acids include 1,2,4-benzenetricarboxylic acid, 1,2,5-benzenetricarboxylic acid, 1,2,4-cyclohexanetricarboxylic acid, 2,5,7-naphthalenetricarboxylic acid, 1,2,4-naphthalenetricarboxylic acid, 1,2,4-butanetricarboxylic acid, 1,2,5-hexatricarboxylic acid, 1,3-dicarboxyl-2-methyl-2-methylenecarboxypropane, tetra(methylenecarboxyl)methane, 1,2,7,8-octanetetracarboxylic acid, and pyromellitic acid. As the derivatives of these trivalent or higher carboxylic acids, lower alkyl esters and acid anhydrides of these carboxylic acids are exemplified.

[0048]

The manufacturing methods of polyester resins are not particularly restricted, and they are manufactured by polycondensation of polyvalent carboxylic acids and polyhydric alcohols by the methods usually used in this industry. In polycondensation, the reacting weight of polyvalent carboxylic acids and polyhydric alcohols is preferably from 0.8 to 1.4 in the molar ratio of hydroxyl group to carboxyl group (OH/COOH). Further, it is preferred to adjust the acid value of the obtained polyester resin to 1 to 100, more preferably from 1 to 30. When the acid value is smaller than 1, the dispersibility

of internal additives, e.g., an electrification controlling agent, a mold releasing agent and a colorant, to the binding resin is reduced. When the acid value is higher than 100, the moisture resistance of the toner lowers. In addition, an acid value is measured by ordinary methods with KOH.

[0049]

When the above polyester resin is used as the binding resin and, in particular, when offset resistance and transparency (smoothness of the fixed image) of a high level are desired, it is preferred to use a urethane-modified polyester resin as the polyester resin.

[0050]

A urethane-modified polyester resin can be obtained by the reaction of a polyester resin with an isocyanate. The reaction is performed by the methods usually used in this industry. In the reaction, it is preferred to blend them so that the isocyanate becomes from 0.3 to 0.99 molar equivalent per molar equivalent of the hydroxyl group of a polyester resin, more preferably from 0.5 to 0.95 molar equivalent. When the molar ratio of the isocyanate is less than 0.3, the offset resistance may decrease. While when the molar ratio is more than 0.99, the viscosity conspicuously increases, so that stirring is sometimes difficult.

[0051]

Isocyanates are not particularly limited, but hexamethylene diisocyanate, isophorone diisocyanate, tolylene diisocyanate, diphenylmethane diisocyanate, xylylene diisocyanate, and tetramethylxylylene diisocyanate are preferably used.

[0052]

The mass average molecular weight of the binding resins which are used in the present invention is not especially restricted, but it is generally preferably from 2,000 to 30,000, more preferably from 4,000 to 25,000, and still more preferably from 6,000 to 20,000. When the molecular weight is less than 2,000, the viscosity lowers at blending, and a colorant cannot be dispersed sufficiently in some cases. Therefore, the chroma or transparency of the obtained toner is liable to lower. When the molecular weight is greater than 30,000, the viscosity becomes too high, so that a colorant cannot be dispersed sufficiently and the chroma or transparency of the toner is sometimes reduced. A plurality of binding resins having the above molecular weight may be mixed.

[0053]

The molecular weight of binding resins is measured by gel permeation chromatography (GPC).

[0054]

When a toner is fixed by thermal fixation in image formation, the flow softening point (T_m) of a binding resin is preferably low. T_m is preferably from 85 to 140°C, more preferably from 90 to 120°C, and still more preferably from 100 to 110°C. The glass transition temperature (T_g) of a binding resin is preferably from 40 to 90°C, more preferably from 50 to 80°C. A flow softening point (T_m) is measured by using a sample obtained by pressure-molding 1.0 g of a binding resin to make a pellet, with "Flow Tester CFT-500D" (a product of Shimadzu Corporation) on conditions of: heat-up velocity of 5°C/min; cylinder pressure of 2.0 MPa; the hole diameter of a die of 1.0 mm; the hole length of a die of 1.0 mm; and by T_m computing method of a 1/2 method. Further, the glass transition temperature (T_g) of a binding resin is measured by packing 10 mg of a binding resin in an aluminum cell and with "DSC120" (a product of Seiko Instruments Inc.) on conditions of: measuring temperature of from 0 to 200°C; and heat-up velocity of 10°C/min; and the value is read from the DSC curve of the second heat-up time.

[0055]

When a toner is fixed by pressure fixation, wax-like resins are preferably used as the binding resin. Of the above binding resins, polyethylene resins, polyethylene-vinyl acetate copolymers and natural waxes are used as the

wax-like resins.

[0056]

The binding resins are manufactured by polymerization, e.g., emulsion polymerization, dispersion polymerization and suspension polymerization, or pulverization including kneading, pulverization and classification processes. Considering the homogeneity and flowability of the finally obtained toner particles, the binding resins obtained by polymerization are preferably used.

[0057]

The binding resins may be used alone or two or more binding resins may be blended. The above-shown binding resins are representative examples and the present invention is not of course limited thereto.

[0058]

(Colorants)

As colorants, the following-shown organic pigments, inorganic pigments and dyes are used. Of organic and inorganic pigments, carbon black, copper oxide, tri-iron tetroxide, manganese dioxide, Aniline Black and active carbon are used as black pigments.

[0059]

As yellow pigments, chrome yellow, zinc yellow, cadmium yellow, yellow iron oxide, mineral fast yellow, nickel titan yellow, naples yellow, Naphthol Yellow S,

Hansa Yellow, Benzidine Yellow G, Benzidine Yellow GR, Quinoline Yellow Lake, Permanent Yellow NCG, and Tartrazine Lake are used.

[0060]

As orange pigments, red chrome yellow, molybdenum orange, Permanent Orange GTR, Pyrazolone Orange, Vulcan Orange, Indanthrene Brilliant Orange RK, Benzidine Orange G, and Indanthrene Brilliant Orange GKM are used.

[0061]

As red pigments, iron oxide red, cadmium red, red lead, mercury sulfide, cadmium, Permanent Red 4R, Lithol Red, Pyrazolone Red, Watchung Red, calcium salt, Lake Red D, Brilliant Carmine 6B, eosine lake, Rhodamine Lake B, Alizarine Lake and Brilliant Carmine 3B are used.

[0062]

As violet pigments, manganese violet, Fast Violet B and Methyl Violet Lake are used. As blue pigments, Prussian blue, cobalt blue, Alkali Blue Lake, Victoria Blue Lake, Phthalocyanine Blue, nonmetal Phthalocyanine Blue, partially chlorinated product of Phthalocyanine Blue, Fast Sky Blue and Indanthrene Blue BC are used.

[0063]

As green pigments, chrome green, chromium oxide, Pigment Green B, Malachite Green Lake and Final Yellow Green G are used.

[0064]

As white pigments, zinc flower, titanium oxide, antimony white and zinc sulfide are used.

[0065]

As extender pigments, baryta powder, barium carbonate, clay, silica, white carbon, talc and alumina white are used.

[0066]

As dyes, basic dyes, acid dyes, dispersed dyes and direct dyes are used. The examples of such dyes include Nigrosine, Methylene Blue, Rose Bengale, Quinoline Yellow and Ultramarine Blue.

[0067]

When the toner of the present invention is a transparent color toner, the following-shown various pigments and dyes are used as the colorants.

[0068]

As yellow pigments, C.I. 10316 (Naphthol Yellow S), C.I. 11710 (Hansa Yellow 10G), C.I. 11660 (Hansa Yellow 5G), C.I. 11670 (Hansa Yellow 3G), C.I. 11680 (Hansa Yellow G), C.I. 11730 (Hansa Yellow GR), C.I. 11735 (Hansa Yellow A), C.I. 11740 (Hansa Yellow NR), C.I. 12710 (Hansa Yellow R), C.I. 12720 (Pigment Yellow L), C.I. 21090 (Benzidine Yellow), C.I. 21095 (Benzidine Yellow G), C.I. 21100 (Benzidine Yellow GR), C.I. 20040 (Permanent Yellow NCG),

C.I. 21220 (Vulcan Fast Yellow 5) and C.I. 21135 (Vulcan Fast Yellow R) are used.

[0069]

As red pigments, C.I. 12055 (Stirling I), C.I. 12075 (Permanent Orange), C.I. 12175 (Lithol Fast Orange 3GL), C.I. 12305 (Permanent Orange GTR), C.I. 11725 (Hansa Yellow 3R), C.I. 21165 (Vulcan Fast Orange GG), C.I. 21110 (Benzidine Orange G), C.I. 12120 (Permanent Red 4R), C.I. 1270 (Para Red), C.I. 12085 (Fire Red), C.I. 12315 (Brilliant Fast Scarlet), C.I. 12310 (Permanent Red F2R), C.I. 12335 (Permanent Red F4R), C.I. 12440 (Permanent Red FRL), C.I. 12460 (Permanent Red FRLL), C.I. 12420 (Permanent Red F4RH), C.I. 12450 (Light Fast Red Toner B), C.I. 12490 (Permanent Carmine FB), and C.I. 15850 (Brilliant Carmine 6B) are used.

[0070]

As blue pigments, C.I. 74100 (nonmetal Phthalocyanine Blue), C.I. 74160 (Phthalocyanine Blue), and C.I. 74180 (Fast Sky Blue) are used.

[0071]

These colorants may be used alone or a plurality of colorants may be used in combination. The colorants are used in an amount of from 1 to 20 mass% to 100 mass% of the binding resin, preferably from 2 to 10 mass%. When the amount of colorants is more than 20 mass%, the fixing

property and transparency of the toner decrease, while when the amount is less than 1 mass%, there is a risk of incapable of obtaining desired image density.

[0072]

(Mold releasing agents)

As the mold releasing agent, paraffin-based waxes, polyolefin-based waxes, modified waxes having an aromatic group, hydrocarbon compounds having an alicyclic group, natural waxes, long chain fatty acids having 12 or more carbon atoms, the esters thereof, metal salts of long chain fatty acids (metal soaps), fatty acid amide and fatty acid bisamide are used. Of the above mold releasing agents, paraffin-based waxes, polyolefin-based waxes and metal soaps are preferably used.

[0073]

The examples of paraffin-based waxes include, e.g., paraffin wax (manufactured by Nippon Oil Co., Ltd. and Nippon Seiro Co., Ltd.), micro-wax (manufactured by Nippon Oil Co., Ltd.), micro-crystalline wax (manufactured by Nippon Seiro Co., Ltd.), hard paraffin wax (manufactured by Nippon Seiro Co., Ltd.), PE-130 (manufactured by Hoechst A.G.), Mitsui High Wax 110P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 220P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 660P (manufactured by Mitsui Petrochemical

Industries, Ltd.), Mitsui High Wax 210P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 320P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 410P (manufactured by Mitsui Petrochemical Industries, Ltd.), Mitsui High Wax 420P (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-1142 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-2130 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-4020 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-1142 (manufactured by Mitsui Petrochemical Industries, Ltd.), modified wax JC-5020 (manufactured by Mitsui Petrochemical Industries, Ltd.), beeswax, carnauba wax and montan wax.

[0074]

As polyolefin-based waxes, e.g., low molecular weight polypropylene, low molecular weight polyethylene, oxidation type polypropylene and oxidation type polyethylene are exemplified. The specific examples of polyolefin-based waxes include non-oxidation type polyethylene waxes, e.g., Hoechst Wax PE520, Hoechst Wax PE130, Hoechst Wax PE190 (manufactured by Hoechst A.G.), Mitsui High Wax 200, Mitsui High Wax 210, Mitsui High Wax 210M, Mitsui High Wax 220, Mitsui High Wax 220M (manufactured by Mitsui Petrochemical Industries, Ltd.),

SANWAX 131-P, SANWAX 151-P, and SANWAX 161-P (manufactured by Sanyo Chemical Industries Co., Ltd.), oxidation type polyethylene waxes, e.g., Hoechst Wax PED121, Hoechst Wax PED153, Hoechst Wax PED521, Hoechst Wax PED522, Hoechst Wax Ceridust 3620, Hoechst Wax Ceridust VP130, Hoechst Wax Ceridust VP5905, Hoechst Wax Ceridust VP9615A, Hoechst Wax Ceridust TM9610F, Hoechst Wax Ceridust 3715 (manufactured by Hoechst A.G.), Mitsui High Wax 420M (manufactured by Mitsui Petrochemical Industries, Ltd.), SANWAX E-300 and SANWAX E-250P (manufactured by Sanyo Chemical Industries Co., Ltd.), non-oxidation type polypropylene waxes, e.g., Hoechst Wachs PP230 (manufactured by Hoechst A.G.), and VISCOL 330-P, VISCOL 550-P, VISCOL 660-P (manufactured by Sanyo Chemical Industries Co., Ltd.), and oxidation type polypropylene waxes, e.g., VISCOL TS-200 (manufactured by Sanyo Chemical Industries Co., Ltd.).

[0075]

As the examples of fatty acid metal salts (metal soaps), e.g., zinc stearate, calcium stearate, magnesium stearate, zinc oleate, zinc palmitate and magnesium palmitate are preferably used.

[0076]

These mold releasing agents may be used alone or a plurality of compounds may be used in combination. Mold releasing agents having a low softening point (melting

point), e.g., from 40 to 130°C, preferably from 50 to 120°C, are preferably used. A softening point is represented by an endothermic main peak value on the DSC endothermic curve measured with "DSC120" (a product of Seiko Instruments Inc.).

[0077]

(Dispersants)

Metal soaps and polyethylene glycol and the like are used as the dispersant.

[0078]

(Electrification controlling agents)

An electrification controlling agent is used for controlling the electrification property of toner mother particles, according to necessity. When the degree of a negative electrification property of a binding resin itself is low or when a binding resin itself is positively electrified, a negative electrification controlling agent is used, so that the toner mother particles at large have a desired level of a negative electrification property.

[0079]

As negative electrification controlling agents, metal salts or metal complexes of salicylic acid derivatives, metal salts of benzilic acid derivatives, and phenyl borate quaternary ammonium salts are exemplified. As the metal salts of salicylic acid derivatives or

benzilic acid derivatives, zinc salts, nickel salts, copper salts and chromium salts of these derivatives are preferably used.

[0080]

The examples of commercially available negative electrification controlling agents include, e.g., Oil Black (Color Index 26150), Oil Black BY (manufactured by Orient Chemical Industry Co., Ltd.), Bontron S-22 (manufactured by Orient Chemical Industry Co., Ltd.), salicylic acid metal complex E-81 (manufactured by Orient Chemical Industry Co., Ltd.), thioindigo series pigments, sulfonylamine derivatives of copper phthalocyanine, Spiron Black TRH (manufactured by HODOGAYA CHEMICAL Co., Ltd.), Bontoron S-34 (manufactured by Orient Chemical Industry Co., Ltd.), Nigrosine SO (manufactured by Orient Chemical Industry Co., Ltd.), Celesschwarz (R)G (manufactured by Farbenfabriken Bayer A.G.), Chromogeneschwarz ETOO (C.I. No. 14645), and Azo Oil Black (R) (manufactured by National Aniline Co.). Of these products, salicylic acid metal complex E-81 is preferably used. These negative electrification controlling agents can be used alone or a plurality of compounds may be used in combination.

[0081]

A negative electrification controlling agent is preferably blended with a binding resin so that the

quantity of electrification of toner mother particles becomes from -5 to -60 $\mu\text{C/g}$. Accordingly, the addition amount of a negative electrification controlling agent is decided by the binding resin used, but generally the amount is from 0.1 to 5 mass parts to 100 mass parts of the binding resin.

[0082]

A positive electrification controlling agent is internally added to a negative electrifiable resin for the purpose of adjusting the quantity of negative electrification of toner mother particles, if necessary. As the positive electrification controlling agents, commercially available products are used. For example, Nigrosine Base EX (manufactured by Orient Chemical Industry Co., Ltd.), a quaternary ammonium salt P-51 (manufactured by Orient Chemical Industry Co., Ltd.), Nigrosine Bontoron N-01 (manufactured by Orient Chemical Industry Co., Ltd.), Sudan Chief Schwarz BB (Solvent Black 3: Color Index 26150), Fetschwarz HBN (C.I. No. 26150), Brilliant Spirits Schwarz TN (manufactured by Farbenfabriken Bayer A.G.), and Zaponschwarz X (manufactured by Farberke Hoechst A.G.) are exemplified. Of these products, a quaternary ammonium salt P-51 is preferably used. In addition to the above products, alkoxylated amine, alkylamide and chelate pigments of molybdic acids are also used as a positive electrification

controlling agent. These positive electrification controlling agents may be used alone or a plurality of compounds may be used in combination.

[0083]

(Magnetic agents)

As magnetic agents, metallic powders of, e.g., Fe, Co, Ni, Cr, Mn and Zn, metallic oxides, e.g., Fe_3O_4 , Fe_2O_3 , Cr_2O_3 , ferrite, and alloys showing ferromagnetism by thermal treatment, e.g., alloys containing manganese and acid, are exemplified. These magnetic agents may be subjected to treatment in advance with a coupling agent.

[0084]

(i-2) Manufacture of toner mother particles:

Toner mother particles are manufactured by adding a colorant and, if necessary, internal additives, e.g., a mold releasing agent, a dispersant, an electrification controlling agent, and a magnetic agent, to a binding resin. A method of manufacturing mother particles by a pulverizing method including kneading, pulverization and classification processes is described below. Firstly, a binding agent, a colorant and additives, e.g., a mold releasing agent, in prescribed amounts are introduced into a mixer, e.g., Henschel Mixer 20B (a product of MITSUI MINING COMPANY, LIMITED) and blended homogeneously. The blending ratios of additives, e.g., a binding resin, a colorant, an

electrification controlling agent, and a mold releasing agent, are decided arbitrarily taking the color and electrification property of the toner into consideration. That is, internal additives are added by considering the electrification property of the toner in a manner such that a negative electrification controlling agent is added to a positively electrifiable binding resin, a negative electrification controlling agent is further added when the electrification property of a negatively electrifiable resin is not sufficient, or a binding resin itself is made negatively electrifiable resin. Particularly when a negatively electrifiable resin is used as a binding resin, it is preferred to adjust the quantity of electrification of toner mother particles to -5 to -60 $\mu\text{C/g}$ as described later.

[0085]

The above mixture is then introduced into a twin-screw kneading extruder (PCM-30, manufactured by IKEGAI KASEI CO., LTD) and homogeneously melt kneaded. As the melt-kneading means besides the above, continuous kneaders, e.g., "TEM-37" (manufactured by TOSHIBA MACHINE CO., LTD.) and "KRC Kneader" (manufactured by KURIMOTO, LTD.), and batch type kneaders, e.g., a hot-pressing kneader, are exemplified. Toner mother particles having a desired average particle size can be obtained by pulverizing the

obtained melt-kneaded product by means of a grinding means. Pulverization is performed by, e.g., impinging pulverization by jet air using a jet pulverizer 200AFG (a product of HOSOKAWA MICRON CORPORATION) or IDS-2 (a product of Nippon Pneumatic Mfg Co., Ltd.), in addition, by a mechanical pulverizer Turbo Mill (a product of Kawasaki Heavy Industries, Ltd.) or Super Rotor (a product of Nisshin Engineering), etc.

[0086]

In the next place, the particle size of the obtained toner mother particles is adjusted by wind power or rotation of rotors. For instance, a sharp particle size distribution can be obtained by using, e.g., a wind power classifier 100ATP (a product of HOSOKAWA MICRON CORPORATION), DSX-2 (a product of Nippon Pneumatic Mfg Co., Ltd.), or Elbow-Jet (a product of NITTETSU MINING CO., LTD.).

[0087]

Toner mother particles may also be manufactured by a method of dissolving internal additives constituting the toner mother particles, e.g., a resin and a colorant, in an organic solvent, dispersing and granulating the aqueous solvent with a classifying agent and an emulsifying agent, and then separating and drying the emulsion.

[0088]

The quantity of electrification of toner mother particles is preferably from -5 to -60 $\mu\text{C/g}$. When the quantity of electrification is smaller than this range, the leakage of the toner from the developing chamber becomes conspicuous, while when the quantity is greater than -60 $\mu\text{C/g}$, there arises a new problem that excess development bias must be given to obtain sufficient image density.

[0089]

For instance, the quantity of electrification of toner mother particles is measured as follows. Under the environment at 25°C, 45% RH, 0.03 g of toner mother particles and 0.97 g of a ferrite carrier are mixed in a polyethylene vessel having a capacity of 20 ml and stirred for 15 minutes at 100 rpm, to thereby electrify the toner mother particles. Subsequently, 0.3 g of the mixture is taken out, and nitrogen gas of the pressure of 0.3 kg/cm^2 is blown to the mixture of the toner mother particles and the carrier, to thereby separate the toner mother particles and the ferrite carrier. After that, the quantity of electrification of every toner (Q/m) is measured and the quantity of electrification of toner mother particles is computed from that. The measurement of the quantity of electrification is performed with, e.g., E-SPART Analyzer (a product of HOSOKAWA MICRON CORPORATION).

[0090]

(ii) Negatively electrifiable silica fine particles:

Negatively electrifiable silica fine particles which are used in the present invention are not particularly restricted. Negatively electrifiable silica fine particles having an average particle size of from 4 to 120 nm, preferably from 5 to 50 nm, and more preferably from 6 to 40 nm are generally used. The smaller the average particle size of negatively electrifiable silica fine particles, the higher is the flowability of the toner obtained. When the average particle size is smaller than 4 nm, the negatively electrifiable silica fine particles are liable to be buried in the toner mother particles. When the average particle size is larger than 120 nm, there is the possibility of conspicuous degradation of the flowability. In the specification of the invention, the terminology "average particle size" of the fine particles of negatively electrifiable silica, positively electrifiable silica, toner mother particles and toner particles means a volume average particle size, unless otherwise indicated.

[0091]

Negatively electrifiable silica fine particles having a uniform average particle size may be used alone, but it is preferred to use two or more negatively electrifiable silica fine particles respectively having different average particle sizes in combination. In

general, negatively electrifiable silica fine particles having a small average particle size (small particle size silica) are used, but when negatively electrifiable silica fine particles having a large average particle size (large particle size silica) are used in combination with small particle size silica, not only the absolute value of the quantity of electrification can be made great, but small particle size silica can be prevented from being buried in toner mother particles due to the resistance of large particle size silica, as compared with the case where small particle size silica is used alone, so that the stability of electrification of the toner can be ensured for a long period of time. Further, it becomes possible to improve the flowability of the toner, and improve the storage stability of the toner by the blocking effect against heat. It is preferred to use negatively electrifiable silica fine particles having an average particle size of from 5 to 20 nm, preferably from 6 to 15 nm, as the small particle size silica and negatively electrifiable silica fine particles having an average particle size of from 20 to 50 nm, preferably from 20 to 40 nm, as the large particle size silica. In addition, the difference in average particle size between large particle size silica and small particle size silica is preferably 10 nm or more, and more preferably 20 nm or more.

[0092]

For the purpose of imparting flowability to a toner and ensuring the stability of electrification for a long period of time, the addition ratio of large particle size silica to small particle size silica in a mass ratio is from 1/3 to 3/1, preferably from 1/2 to 2/1, and more preferably from 1/1.5 to 1.5/1.

[0093]

When large particle size silica and small particle size silica are used together, two kinds of silica particles may be blended at the same time, alternatively either silica particles may be added prior to the other in the manufacture of a toner as described later.

[0094]

The addition amount of negatively electrifiable silica fine particles is variable according to the particle size distribution or flowability of toner mother particles, the particle size distribution of external additives, and a desired quantity of electrification. For instance, the above small particle size silica is added in an amount of from 0.5 to 2.0 mass parts to 100 mass parts of the toner mother particles, and preferably from 0.7 to 1.5 mass parts. In the case of large particle size silica, the addition amount is from 0.2 to 2.0 mass parts to 100 mass parts of the toner mother particles, and preferably from 0.3 to 1.5

mass parts. When large particle size silica and small particle size silica are used in combination, they are added in total amount of from 0.5 to 3.0 mass parts to 100 mass parts of the toner mother particles, preferably from 0.7 to 2.5 mass parts, taking the above-described blending ratio into consideration.

[0095]

It is preferred that negatively electrifiable silica fine particles be subjected to hydrophobitization treatment. By making the surfaces of negatively electrifiable silica fine particles hydrophobic, the flowability and electrification property of the toner are further improved. The hydrophobitization treatment of silica fine particles is carried out according to wet methods or dry methods usually used in the industry with a silane compound, e.g., aminosilane, hexmethyldisilazane, or dimethyldicyclosilane; or a silicone oil, e.g., dimethylsilicone, methylphenylsilicone, fluorine-modified silicone oil, alkyl-modified silicone oil, amino-modified silicone oil, or epoxy-modified silicone oil.

[0096]

As negatively electrifiable hydrophobic silica fine particles, commercially available RX200 and RX50 (manufactured by Nippon Aerosil Co., Ltd.) and TG811F, TG810G and TG308F (manufactured by Cabot) are used.

[0097]

(iii) Positively electrifiable silica fine particles:

Positively electrifiable silica fine particles which are used in the present invention are not especially limited. The volume average particle size of positively electrifiable silica fine particles is preferably from 10 to 50 nm, more preferably from 15 to 40 nm, taking the flowability and the like into consideration.

[0098]

In manufacturing a toner as described later, positively electrifiable silica fine particles are added in an amount of from 0.1 to 1.0 mass part to 100 mass parts of the toner mother particles, preferably from 0.2 to 0.8 mass parts.

[0099]

When a negatively electrifiable resin is used as the binding resin and negatively electrifiable silica fine particles are not used as the electrification controlling agent, positively electrifiable silica fine particles are added in an amount of from 0.1 to 2.0 mass parts to 100 mass parts of the toner mother particles, preferably from 0.3 to 1.5 mass parts.

[0100]

It is preferred that positively electrifiable silica fine particles be subjected to hydrophobitization treatment.

By making the surfaces of positively electrifiable silica fine particles hydrophobic, the fluctuation of the electrification property of the toner due to the changes in external environment can be lessened (that is, a stable electrification property can be maintained), and the flowability of the toner can be improved. The hydrophobitization of positively electrifiable silica fine particles is carried out according to the same method as the hydrophobitization of negatively electrifiable silica fine particles.

[0101]

As positively electrifiable hydrophobic silica fine particles, commercially available NA50H (manufactured by Nippon Aerosil Co., Ltd.) and TG820F (manufactured by Cabot) are used.

[0102]

(iv) Titanium oxide (titania) fine particles:

Titanium oxide fine particles for use in the present invention are not particularly limited. Titanium oxide fine particles having a relatively small electrical resistivity are preferably used. Titanium oxide may take a crystal form of rutile type, anatase type, rutile-anatase type. Titanium oxide of any crystal form may be used, but titanium oxide of a rutile-anatase type is preferably used for the reason that the adjustment of electric charge is

easy and a rutile-anatase type titanium oxide is difficult to be buried in toner mother particles even when the number of sheets of printing increases.

[0103]

The size of titanium oxide fine particles is not particularly restricted but it is preferred that the particle size or long axis length be 10 to 30 nm. In the case of a rutile-anatase type titanium oxide, titanium oxide fine particles having a long axis length of from 10 to 30 nm or so are preferred.

[0104]

Titanium oxide fine particles are used in an amount of from 0.2 to 2.0 mass parts to 100 mass parts of the toner mother particles, preferably from 0.3 to 1.5 mass parts. The mass ratio of titanium oxide fine particles to positively electrifiable silica fine particles is preferably from 1/3 to 3/1 from the point of capable of adjusting electric charge without causing extreme reduction of electrical resistance of the toner.

[0105]

By making the surfaces of titanium oxide fine particles hydrophobic, the fluctuation of the electrification property of the toner due to the changes in external environment can be lessened (that is, a stable electrification property can be maintained), and the

flowability of the toner can be improved. The hydrophobitization of titanium oxide fine particles is carried out according to the same method as the hydrophobitization of negatively electrifiable silica fine particles.

[0106]

As hydrophobic titanium oxide fine particles, STT-30S (manufactured by TITAN KOGYO KABUSHIKI KAISHA) and the like are used.

[0107]

(v) Long chain fatty acid or salt thereof

The long chain fatty acids or salts thereof for use in the present invention are not particularly restricted. As the long chain fatty acids, long chain fatty acids preferably having from 10 to 30 carbon atoms, more preferably from 12 to 28, and most preferably from 12 to 18, are used. As the long chain fatty acids, long chain saturated fatty acids and long chain unsaturated fatty acids are exemplified. Long chain saturated fatty acids are preferably used. The long chain fatty acids may be branched, but long chain saturated fatty acids, e.g., stearic acid, is preferably used.

[0108]

It is preferred to use the long chain fatty acids in the form of salts, and more preferably in the form of metal

salts (so-called metal soaps). The metal salts of the long chain fatty acids are not particularly restricted and, e.g., calcium salts, zinc salts, magnesium salts, aluminum salts and lithium salts are exemplified. As the metal soaps, e.g., magnesium stearate, calcium stearate and zinc stearate are exemplified, and fine particles of these metal soaps are preferably used. Particles comprising long chain saturated fatty acids or salts thereof may be used alone or as mixtures of two or more kinds.

[0109]

Long chain fatty acids or salts thereof, particularly long chain fatty acid metal salts (metal soaps) have a volume average particle size or long axis size of preferably from 0.5 to 10 μm , more preferably from 1 to 5 μm . When the volume average particle size or long axis size deviates from this range, the long chain fatty acids or salts thereof cannot show the effects as the binder, lubricant and auxiliary flowing agent, or the coagulation of the toner cannot be sufficiently inhibited.

[0110]

It is preferred for the long chain fatty acids or salts thereof, particularly metal soaps to have a melting point of from 100 to 150°C or so in view of heat resistance and lubricating ability. When the melting point is lower than 100°C, the heat resistance of the toner lowers, and

there is the possibility of the coagulation of the toner when stored under the high temperature environment. When the melting point is higher than 150°C, the lubricating function of the toner is liable to decrease.

[0111]

As metal soaps, metal soaps manufactured by a direct method and metal soaps manufactured by a double decomposition method are known, and it is preferred to use metal soaps manufactured by a direct method containing less impurities by pulverizing and adjusting the particle sizes so as to reach the above average particle size.

[0112]

The addition amount of the long chain fatty acids or salts thereof, particularly particles comprising long chain saturated fatty acids or salts thereof, is from 0.1 to 1.0 mass part to 100 mass parts of the toner mother particles, preferably from 0.1 to 0.5 mass parts. When the addition amount is less than 0.1 mass%, the effect as the binder cannot be exhibited, coagulation of the toner cannot be prevented, and the effects as auxiliary flowing agent and lubricant cannot be sufficiently shown. When the addition amount is higher than 1.0 mass%, the flowability reduces, start-up of electrification conspicuously deteriorates, so that there is the possibility of generation of noise such as fog.

[0113]

(vi) Inorganic fine particles

Inorganic fine particles other than titanium oxide fine particles are also externally added for the purpose of controlling the electrification property and improving flowability. For instance, as inorganic fine particles, fine particles of metallic oxide, e.g., aluminum oxide, strontium oxide, tin oxide, zirconia oxide, magnesium oxide, and indium oxide; fine particles of nitrides, e.g., silicon nitride; fine particles of carbides, e.g., silicon carbide; fine particles of metal salts, e.g., calcium sulfate, barium sulfate and calcium carbonate; and inorganic fine particles of these are exemplified. Fine particles of metallic oxides having a relatively small electrical resistivity, e.g., $10^9 \Omega\text{-cm}$ or less are preferably used.

[0114]

The sizes of inorganic fine particles added are not particularly restricted, but the sizes of from 10 to 30 nm are preferred. It is preferred that the surfaces of these inorganic fine particles be subjected to hydrophobitization treatment for the purpose of improving the stabilization of electrification characteristics. The hydrophobitization treatment of inorganic fine particles is performed by the same method as used in the hydrophobitization treatment of negatively electrifiable silica fine particles or

positively electrifiable silica fine particles.

[0115]

(II) Toner of the present invention and manufacturing method:

The toner in the invention is a toner obtained by adding external additives to toner mother particles by multistage process, and particles comprising at least a long chain fatty acid or a salt thereof are added in the final stage of the multistage process. The terminology "particles comprising at least a long chain fatty acid or a salt thereof are added" means not only the case where only a long chain fatty acid or a salt thereof are added alone, but also the case where external additives other than the external additives which have been already added are added with a long chain fatty acid or a salt thereof.

[0116]

As described above, the toner of the invention is characterized in that the toner is obtained by adding a long chain fatty acid or a salt thereof in the final stage of multistage process. It is thought that by adding a long chain fatty acid or a salt thereof finally, the long chain fatty acid or a salt thereof functions as the binder of external additives, such as negatively electrifiable silica fine particles, positively electrifiable silica fine particles and titanium oxide fine particles, and prevents

the desorption of these external additives from the surfaces of the toner. It is also thought that by adding a long chain fatty acid or a salt thereof finally, the effect as the lubricant of the toner is further brought out and uniform electrification can be maintained. Further, in repeating use, the stability of electrification can be maintained. This is presumed to be the result that the long chain fatty acid or a salt thereof prevents the coagulation of the toner as the lubricant, and the external additives are prevented from being buried in toner mother particles due to the friction of toner particles. Furthermore, it is thought that the toner is brought into contact with the photosensitive material in the developing chamber, thereby the long chain fatty acid or a salt thereof migrates to the surface of the photosensitive material and lubricates the surface of the photosensitive material, as a result, the photosensitive material is prevented from being abraded by the external additives on the surface of the toner.

[0117]

Further, the toner of the invention exhibits further effects by adopting multistage process as compared with conventional toners which are obtained by the external addition of external additives and a long chain fatty acid or a salt thereof by one time process, or toners which are

obtained by adding external additives after the addition of a long chain fatty acid or a salt thereof.

[0118]

(II-1) A case where toner mother particles are positively electrifiable to weakly negatively electrifiable:

In performing multistage process when toner mother particles are positively electrifiable to weakly negatively electrifiable, it is preferred that external additives to be added first be negatively electrifiable silica fine particles, negatively electrifiable silica fine particles and titanium oxide fine particles, or titanium oxide fine particles. These processes are described in (II-1-1) to (II-1-3) below.

[0119]

(II-1-1) Toner obtained by the addition of negatively electrifiable silica fine particles first:

When negatively electrifiable silica fine particles are added alone, the static attraction between the toner mother particles and the negatively electrifiable silica fine particles is not hindered by positively electrifiable silica fine particles, and the difference between the work function of the negatively electrifiable silica fine particles and the work function of the toner mother particles is large, so that the negatively electrifiable silica fine particles can be strongly adhered to the toner

mother particles. Therefore, the desorption of the negatively electrifiable silica fine particles is prevented, the fluctuation of electrification property lessens, as a result, the electrification property can be stabilized for a long period of time. It is preferred to use small particle size silica and large particle size silica in combination as the negatively electrifiable silica fine particles, for the reasons that the absolute value of the quantity of electrification can be made great, electrification stability can be obtained for a long period of time, and it becomes possible to heighten the storage stability of the toner by improving the flowability of the toner and exhibiting the blocking effect against heat.

[0120]

When negatively electrifiable silica fine particles are added first, titanium oxide fine particles and positively electrifiable silica fine particles are added in the next place. Titanium oxide fine particles and positively electrifiable silica fine particles may be added at the same time, but it is preferred to add titanium oxide fine particles prior to the addition of positively electrifiable silica fine particles. Positively electrifiable silica fine particles are positively electrified and have high electrical resistivity. Therefore, by adding titanium oxide fine particles in

advance and then adding positively electrifiable silica fine particles, the positively electrifiable silica fine particles function as the electric charge adjuster, and the reduction of the electrical resistivity of the toner is controlled and the electric charge is unified. Further, since the positively electrifiable silica fine particles come to be liberated and present in the toner in an appropriate rate, the flowability of the toner becomes good and, at the same time, the free positively electrifiable silica fine particles function as the carrier, so that the electrification property becomes more uniform.

[0121]

There are four-stage process of adding, to toner mother particles, in the order of negatively electrifiable silica fine particles, titanium oxide fine particles, then positively electrifiable silica fine particles alone, and finally particles comprising a long chain fatty acid or a salt thereof; and three-stage process of adding positively electrifiable silica fine particles and particles comprising a long chain fatty acid or a salt thereof in the above third and fourth stages simultaneously as the final stage. Further, these external additives may be added in two-stage process of adding titanium oxide fine particles, positively electrifiable silica fine particles and particles comprising a long chain fatty acid or a salt

thereof simultaneously to negatively electrifiable silica fine particles. Above all, three-stage process of adding positively electrifiable silica fine particles and particles comprising a long chain fatty acid or a salt thereof simultaneously is preferred for the reason that the adjustment of surface electric charge by positively electrifiable silica fine particles and titanium oxide fine particles can be most efficiently performed without extremely reducing the electrical resistance.

[0122]

As multistage process of adding negatively electrifiable silica fine particles first and finally at least a long chain saturated fatty acid or a salt thereof, e.g., multistage processes of the following (a) to (f) are exemplified: (a) negatively electrifiable silica fine particles - titanium oxide fine particles - positively electrifiable silica fine particles - a long chain saturated fatty acid or a salt thereof; (b) negatively electrifiable silica fine particles - titanium oxide fine particles - (positively electrifiable silica fine particles + a long chain saturated fatty acid or a salt thereof); (c) negatively electrifiable silica fine particles - titanium oxide fine particles - a long chain saturated fatty acid or a salt thereof; (d) negatively electrifiable silica fine particles - (titanium oxide fine particles + a long chain

saturated fatty acid or a salt thereof); (e) negatively electrifiable silica fine particles - (titanium oxide fine particles + positively electrifiable silica fine particles); and (f) negatively electrifiable silica fine particles - positively electrifiable silica fine particles - a long chain saturated fatty acid or a salt thereof.

[0123]

As described above, the toner obtained by adding negatively electrifiable silica fine particles first and a long chain fatty acid or a salt thereof in the final stage shows the effect of strong adhesion of the negatively electrifiable silica fine particles to the toner mother particles, and the effects by the final addition of the long chain fatty acid or a salt thereof are exhibited, therefore, the toner has excellent properties, such that the liberation of the silica fine particles is controlled and a uniform electrification property is maintained for a long period of time, as compared with conventional toners which are obtained by one time process.

[0124]

(II-1-2) Toner obtained by the addition of negatively electrifiable silica fine particles and titanium oxide fine particles first:

Negatively electrifiable silica fine particles and titanium oxide fine particles may be added to toner mother

particles at the same time in the first place. Since the negatively electrifiable silica fine particles relatively strongly adhere to the toner mother particles from the relationship between the work function of the negatively electrifiable silica fine particles, the work function of the titanium oxide fine particles, and the work function of the toner mother particles, the liberation of the silica fine particles is controlled. In addition, the effects due to the final addition of the long chain saturated fatty acid or a salt thereof are exhibited.

[0125]

As such multistage process, (g) (negatively electrifiable silica fine particles + titanium oxide fine particles) - positively electrifiable silica fine particles - a long chain saturated fatty acid or a salt thereof; and (h) (negatively electrifiable silica fine particles + titanium oxide fine particles) - (positively electrifiable silica fine particles + a long chain saturated fatty acid or a salt thereof) are exemplified.

[0126]

(II-1-3) Toner obtained by the addition of titanium oxide fine particles first:

When titanium oxide fine particles are added first, it is preferred to add negatively electrifiable silica fine particles in the next place. This is due to consideration

of strongly adhering negatively electrifiable silica fine particles to toner mother particles in the first place, thinking the respective work functions of toner mother particles, positively electrifiable silica fine particles and negatively electrifiable silica fine particles. In the next place, according to necessity, by adding positively electrifiable silica fine particles prior to, or simultaneously with, a long chain fatty acid or a salt thereof, the quantity of electrification can be adjusted with preventing the sudden reduction of the quantity of electrification. In addition to this effect, the effects by the long chain fatty acid or a salt thereof are exhibited.

[0127]

As such multistage process, (i) titanium oxide fine particles - negatively electrifiable silica fine particles - positively electrifiable silica fine particles - a long chain saturated fatty acid or a salt thereof; (j) titanium oxide fine particles - negatively electrifiable silica fine particles - (positively electrifiable silica fine particles + a long chain saturated fatty acid or a salt thereof); and (k) titanium oxide fine particles - negatively electrifiable silica fine particles - a long chain saturated fatty acid or a salt thereof; are exemplified.

[0128]

(II-2) A case where toner mother particles are negatively electrified:

When toner mother particles are negatively electrified, it is preferred for the negatively electrifiable toner mother particles to have the quantity of electrification of from -5 to -60 $\mu\text{C/g}$. In multistage process of the negatively electrified toner mother particles, negatively electrifiable silica fine particles are not generally used. However, when the degree of negative electrification is weak, negatively electrifiable silica fine particles are used at times for the purpose of adjusting the electric charge. External additives are added so that the quantity of electrification of the toner obtained generally becomes from -7 to -30 $\mu\text{C/g}$.

[0129]

When negatively electrifiable toner mother particles are used, multistage process of adding positively electrifiable silica fine particles first; adding positively electrifiable silica fine particles and other external additives first; and adding titanium oxide fine particles first are exemplified. These processes are described in (II-2-1) to (II-2-3) below.

[0130]

(II-2-1) Toner obtained by the addition of positively electrifiable silica fine particles first:

It is most preferred to add positively electrifiable silica fine particles first. According to the process, the static attraction between the negatively electrifiable toner mother particles and the positively electrifiable silica fine particles is not hindered, and the difference between the work function of the positively electrifiable silica fine particles and the work function of the toner mother particles is large, so that the positively electrifiable silica fine particles are strongly adhered to the toner mother particles. Therefore, the desorption of the positively electrifiable silica fine particles is prevented, the fluctuation of the electrification property lessens, as a result, the electrification property can be stabilized for a long period of time.

[0131]

After the addition of positively electrifiable silica fine particles, titanium oxide fine particles are added alone or together with particles comprising a long chain fatty acid or a salt thereof. By adding positively electrifiable silica fine particles having a high electrical resistance value in advance, the surface electric charge of the toner does not lower greatly when titanium oxide fine particles low in electrical resistance are added (that is, the positively electrifiable silica fine particles function as the electric charge adjuster),

the reduction of the electrical resistivity of the toner is controlled and the electric charge is unified. In addition to these effects, the effects due to the final addition of the long chain fatty acid or a salt thereof are exhibited.

[0132]

As such multistage process, (l) positively electrifiable silica fine particles - a long chain fatty acid or a salt thereof; and (m) positively electrifiable silica fine particles - (titanium oxide fine particles + a long chain fatty acid or a salt thereof) are exemplified.

[0133]

Negatively electrifiable toner mother particles are not contained as the external additive in this multistage process. A toner not containing negatively electrifiable toner mother particles as the external additive has good electrification properties and good flowability. This toner has advantages that the fixing temperature of the toner can be made low (the fixing temperature in a fixing chamber can be set low), and the fixing strength of the image after fixation is satisfactory.

[0134]

(II-2-2) Toner obtained by the addition of positively electrifiable silica fine particles and other external additives first:

When other external additive is negatively electri-

fiabile silica fine particles, considering that the toner mother particles are negatively electrified, it is preferred from the point of electrification control to add positively electrifiable silica fine particles at the same time with negatively electrifiable silica fine particles in the first place. As multistage process of adding positively electrifiable silica fine particles and negatively electrifiable silica fine particles in the first place, (n) (positively electrifiable silica fine particles + negatively electrifiable silica fine particles) - titanium oxide fine particles - a long chain fatty acid or a salt thereof; (o) (positively electrifiable silica fine particles + negatively electrifiable silica fine particles + titanium oxide fine particles) - a long chain fatty acid or a salt thereof; and (p) (positively electrifiable silica fine particles + negatively electrifiable silica fine particles) - a long chain fatty acid or a salt thereof, are exemplified.

[0135]

In the above example (p) of multistage process, titanium oxide fine particles are not added, but when the quantity of electrification is in a proper range, they may not be added.

[0136]

(II-2-3) Toner obtained by the addition of titanium oxide

fine particles first:

Titanium oxide fine particles may be added first, and as such multistage process, (q) titanium oxide fine particles - negatively electrifiable silica fine particles - positively electrifiable silica fine particles - a long chain fatty acid or a salt thereof; and (r) titanium oxide fine particles - negatively electrifiable silica fine particles - (positively electrifiable silica fine particles + a long chain fatty acid or a salt thereof) are exemplified.

[0137]

The orders in the above multistage processes (a) to (r) are exemplifications and the present invention is not limited thereto. In addition, if necessary, inorganic fine particles described in the above (vi) may be added with a view to adjusting electric charge and improving flowability. Inorganic fine particles may be added in any stage provided that they are added before or simultaneously with the addition of a long chain fatty acid or a salt thereof.

[0138]

As described above, the external additives of the toner of the present invention are strongly adhered to toner mother particles in multistage process by the work function of each external additive and the work function of toner mother particles, and the liberation controlling

effect of external additives is further reinforced by the binding function of the long chain fatty acid or a salt thereof added in the final stage. Further, uniformity of electrification and long term stability of electrification are strengthened, and the stability of electrification is maintained in repeating use. In addition, preventing effect of coagulation of toner, and the effects as auxiliary flowing agent and lubricant can be sufficiently shown. Further, it is thought that the toner is brought into contact with the photosensitive material, as a result the long chain fatty acid or a salt thereof migrates to the surface of the photosensitive material and lubricates the surface of the photosensitive material, thereby the effect of preventing a photosensitive material from being abraded by the external additives on the surface of the toner is further heightened.

[0139]

On the other hand, conventional toners, e.g., the toners disclosed in patent literature 1 to 4, are toners obtained by externally adding positively electrifiable silica fine particles and negatively electrifiable silica fine particles at the same time, and it is thought that by adding positively electrifiable silica fine particles and negatively electrifiable silica fine particles at the same time, the static attraction between the toner mother

particles and the negatively electrifiable silica fine particles becomes small, as a result, the desorption of the negatively electrifiable silica fine particles are liable to occur. Further, it is also presumed that since conventional toners do not contain a long chain fatty acid or a salt thereof, the liberation of negatively electrifiable and/or positively electrifiable silica fine particles or titanium oxide fine particles cannot be restrained.

[0140]

Addition of negatively electrifiable silica fine particles, titanium oxide fine particles, positively electrifiable silica fine particles and a long chain fatty acid or a salt thereof to toner mother particles is carried out by machines or methods usually used in this industry, e.g., high speed fluid mixers, such as a Henschel mixer or Perpenmyer, and mixers using a mechanochemical method. The velocity and time of stirring in each process of multistage process can be set independently, but the conditions may be the same.

[0141]

The toner of the invention can be used in any type of image-forming apparatus, e.g., image-forming apparatus using one-component series toners, or image-forming apparatus using two-component series toners, may be used.

Image-forming apparatus of a contact development system or image-forming apparatus of a non-contact development system may also be used. Image-forming apparatus of a contact development system using one-component series toners capable of using the toner of the invention are described in detail, e.g., in patent literature 13. The image-forming apparatus of the present invention is equipped with at least a latent image carrier on which an electrostatic latent image is formed represented by a photosensitive material; a toner carrier for carrying a toner to the latent image carrier for developing the electrostatic latent image on the latent image carrier represented by a developing roller; and a developing chamber having a toner regulating member to regulate the amount of the toner carried to the latent image carrier by the toner carrier. The toner of the present invention is held in a toner holder, carried from the toner holder to the developing roller (the toner carrier) and supplied to the photosensitive material (the latent image carrier) via the developing roller (the toner carrier), transferred, thereby an image is formed. The toner regulating member adjusts the amount of the toner so that an excess amount of the toner is not supplied to the photosensitive material (the latent image carrier) from the developing roller (the toner carrier).

[0142]

[Example]

The present invention is illustrated with reference to examples below. In the first place, the evaluation methods in the present invention are described. Items and methods of evaluations are as follows.

[0143]

1. Liberation rate of external additives (silica fine particles, titanium oxide fine particles):

The liberation rate of external additives (silica fine particles and titanium oxide fine particles) was measured with PT100 Particle Analyzer (a product of Yokogawa Electric Corporation). The details of measuring method of the liberation rate of external additives are disclosed in patent literature 13 (JP-A-2002-202622). Describing the principle in brief, liberation rate is obtained by introducing toner particles into plasma, exciting the toner particle to emit light, and measuring the intensity and time of the emission. For example, toner particles to which external additive SiO_2 has been added are introduced into plasma, and the emission intensity of SiO_2 in the toner particles is measured. Assuming that the toner particle to which SiO_2 has been externally added is a spherical particle, the particle size of the spherical particle (equivalent particle size) is obtained from the

emission intensity. Similarly to the case of the toner particle, the equivalent particle size of the liberated SiO_2 can be obtained from the emission intensity. However, since the emission intensity of the liberated SiO_2 is small, the equivalent particle size is small. Accordingly, the liberated external additive can be distinguished from the toner particles by comparing equivalent particle sizes. Therefore, the liberation rate of SiO_2 can be obtained according to the following equation (X), by obtaining all the detected number of external additive SiO_2 , and taking the number of individuals having smaller equivalent particle size as the number of particles of the liberated external additive.

[0144]

[mathematical formula 1]

Liberation rate = (detected number of liberated external additive/all detected number of external additive) x 100 (%) (X)

[0145]

Whether SiO_2 is adhered to a toner particle or liberated is distinguished by making use of the fact that SiO_2 adhered to a toner particle emits light synchronously with the toner particle, but SiO_2 which is not adhered to a toner particle does not radiate synchronously with the toner particle and the time of emission deviates from that

of the toner particle (asynchronously). On the basis of the measured value, the liberation rate can be obtained by the following equation (Y).

[0146]

[mathematical formula 2]

Liberation rate = (asynchronous count of external additive/asynchronous count + synchronous count of external additive) x 100 (%) (Y)

[0147]

A method represented by equation (Y) was adopted in the present invention. In addition, the measurement of the liberation rate of titanium oxide fine particles is performed in the same manner as above by exciting titanium oxide fine particles to emit light in plasma. The volume average particle size of toner mother particles can also be obtained, e.g., by making a colorant contained in the toner mother particles emit light in plasma, and obtaining the equivalent particle size.

[0148]

2. Uniformity of quantity of electrification and electrification:

The quantity of electrification of a toner is measured as follows with E-SPART Analyzer (manufactured by HOSOKAWA MICRON CORPORATION). Each of the toners prepared in Examples and Comparative Examples and carrier were mixed

and stirred, to thereby electrify the toner. Nitrogen gas was then blown to the mixture of the toner and the carrier to separate the toner and the carrier. In the next place, the quantity of electrification of every toner (Q/m) was measured, and the distribution of the quantities of electrification of the toners was obtained. The uniformity of electrification is judged as follows. In number distribution of the quantity of electrification of every one toner (Q/m), the difference between the quantity of electrification of the maximum frequency (Q_1/m_1) and the value obtained by dividing the total quantity of electrification of the measured toners by the measured count (the number) (Q_2/m_2), i.e., the smaller the absolute value of $(Q_1/m_1) - (Q_2/m_2)$, the sharper is the distribution of the quantity of electrification (uniform), and the greater the absolute value of $(Q_1/m_1) - (Q_2/m_2)$, the broader is the distribution of the quantity of electrification (nonuniform).

[0149]

As the carrier, KBN100 ferrite carrier (manufactured by Hitachi Metals, Ltd.) was used.

[0150]

3. Electrical resistivity of toner:

Electrical resistivity was measured with a hybrid type electrical resistivity tester model DRT-1

(manufactured by Sankyo Biotics according to JIS B9915.

[0151]

4. Durability test:

A copier (model LP-9300 manufactured by Seiko Epson Corporation) was charged with a toner, and printing of 3,000 sheets was performed. Printing was begun when 5% of the toner was consumed, and the distribution of electrification, electrical resistivity and the liberation rate of the external additives before and after printing were measured.

[0152]

(Preparation of toner mother particles)

One hundred (100) mass parts of a binding resin comprising styrene-acrylic-based resin or a polyester resin, 3.5 mass parts of a red pigment (C.I. 12055), and 1.0 mass part of chromium salicylate complex were put into Henschel Mixer 20B (a product of MITSUI MINING COMPANY, LIMITED), and homogeneously blended. The mixture was melt-kneaded with a two-shaft kneading extruder PCM-30 (manufactured by IKGAI KASEI CO., LTD), and after cooling, pulverized by jet air with a jet pulverizer 200AFG (a product of HOSOKAWA MICRON CORPORATION). The pulverized product was classified with a wind power classifier 100ATP (a product of HOSOKAWA MICRON CORPORATION), to thereby prepare toner mother particles having a volume average particle size of 8.5 μm .

[0153]

(External additives)

The external additives externally added to toner mother particles in Examples are shown in Table 1 below.

[0154]

Table 1

	External Additive	Trade Name	Average Particle Size	Manufacturer
a1	Negatively electrifiable silica	Negatively electrifiable hydrophobic silica RX200	15 nm	Nippon Aerosil Co., Ltd.
a2	Negatively electrifiable silica	Negatively electrifiable hydrophobic silica RX50	40 nm	Nippon Aerosil Co., Ltd.
b	Titanium oxide	Hydrophobic titanium oxide*) STT-30S	Long axis: 20 nm	TITAN KOGYO KABUSHIKI KAISHA
c	Positively electrifiable silica	Positively electrifiable hydrophobic silica NA50H	30 nm	Nippon Aerosil Co., Ltd.
d	Long chain fatty acid salt	Magnesium stearate		

*) Rutile-anatase type

[0155]

(Examples 1-13 and Comparative Example 1-7)

Examples 1-13 and Comparative Examples 1 to 7 was obtained by adding external additives shown in Table 2 below each in the prescribed amount and prescribed order as shown in Table 2 to 100 mass parts of toner mother particles comprising a styrene-acrylic resin as the binding resin. The process of external addition was performed by using Henschel Mixer FM20B (a product of MITSUI MINING COMPANY, LIMITED), and stirring the external additives for 3 minutes with ZOSO type stirring blades, at 2,000 rpm. The process of external addition in each stage was performed on the same condition. The external additives used, the amounts and the addition order are shown in Table 2.

[0156]

Table 2

	External Additives					Order of External Addition			
	a1	a2	b	c	d	First Stage	Second Stage	Third Stage	Fourth Stage
Example 1	1.0	-	0.5	0.5	0.1	a1	b	c	d
Example 2	1.0	-	0.5	0.5	0.1	a1	b	c+d	-
Example 3	0.5	0.5	0.5	0.5	0.1	a1+a2	b	c+d	-
Example 4	1.0	-	1.0	-	0.2	a1	b	d	-
Example 5	1.0	-	1.0	-	0.2	a1	b+d	-	-
Example 6	1.0	-	1.0	0.5	0.1	a1	b+c+d	-	-
Example 7	0.5	0.5	1.0	0.5	0.1	a1+a2	b+c+d	-	-
Example 8	1.0	-	0.5	0.5	0.2	a1+b	c	d	-
Example 9	1.0	-	0.5	0.5	0.2	a1+b	c+d	-	-
Example 10	1.0	-	0.5	0.5	0.2	b	a1	c	d
Example 11	1.0	-	0.5	0.5	0.2	b	a1	c+d	-
Example 12	1.0	-	0.5	-	0.2	b	a1	d	-
Example 13	1.0	-	-	0.5	0.2	a1	c	d	-
Comparative Example 1	1.0	-	0.5	0.5	-	a1+b+c	-	-	-

Comparative Example 2	1.0	-	0.5	0.5	-	a1	c	b	-
Comparative Example 3	1.0	-	0.5	-	-	a1	b	-	-
Comparative Example 4	1.0	-	0.5	0.5	0.1	a1+b+c+d	-	-	-
Comparative Example 5	1.0	-	1.0	-	-	a1	b	-	-
Comparative Example 6	1.0	-	1.0	-	0.2	a1+b+c	-	-	-
Comparative Example 7	0.5	0.5	1.0	0.5	0.1	a1+a2+b+c+d	-	-	-

The numeral in the column of External Additives shows the addition amount (mass parts) to 100 mass parts of toner mother particles.

[0157]

The toners obtained in Table 2 above were evaluated according to the evaluation methods described above. The results obtained are shown in Table 3 below.

[0158]

Table 3

	(i)	(ii)	(iii)	Electrical Resistivity ($\Omega\cdot\text{cm}$)	Liberation Rate of Silica (%)	Liberation Rate of Titanium Oxide (%)
	Q_1/m_1 ($\mu\text{C/g}$)	Q_2/m_2 ($\mu\text{C/g}$)	(i)-(ii) ($\mu\text{C/g}$)			
Example 1	-11.86	-12.26	0.40	4.3×10^{16}	0.38	0.46
Example 2	-11.53	-11.66	0.13	4.4×10^{16}	0.38	0.51
Example 3	-11.56	-11.69	0.13	4.1×10^{16}	0.39	0.43
Example 4	-12.34	-14.26	1.92	-	0.42	0.53
Example 5	-12.56	-13.03	0.47	-	0.32	0.47
Example 6	-12.12	-16.11	3.99	4.3×10^{16}	0.39	0.49
Example 7	-13.15	-16.63	3.48	4.1×10^{16}	0.41	0.56
Example 8	-11.22	-12.56	1.44	4.7×10^{16}	0.35	0.48
Example 9	-12.69	-13.11	0.42	4.2×10^{16}	0.36	0.47
Example 10	-13.52	-14.62	1.10	4.2×10^{16}	0.45	0.37
Example 11	-14.62	-15.88	1.26	4.2×10^{16}	0.48	0.44
Example 12	-14.89	-16.21	1.32	4.2×10^{16}	0.37	0.46
Example 13	-11.63	-13.51	1.88	4.2×10^{16}	0.51	0.48

	(i)	(ii)	(iii)	Electrical Resistivity ($\Omega \cdot \text{cm}$)	Liberation Rate of Silica (%)	Liberation Rate of Titanium Oxide (%)
	Q_1/m_1 ($\mu\text{C/g}$)	Q_2/m_2 ($\mu\text{C/g}$)	(i)-(ii) ($\mu\text{C/g}$)			
Comparative Example 1	-12.96	-16.31	3.35	4.5×10^{16}	0.46	1.28
Comparative Example 2	-13.44	-20.68	7.24	7.9×10^{15}	0.38	0.98
Comparative Example 3	-12.96	-16.31	3.35	4.5×10^{16}	0.46	1.28
Comparative Example 4	-13.53	-15.89	2.36	-	0.55	0.89
Comparative Example 5	-13.72	-19.23	5.51	-	0.61	0.89
Comparative Example 6	-9.22	-15.89	6.67	8.9×10^{15}	0.78	0.79
Comparative Example 7	-18.74	-22.56	3.82	4.5×10^{16}	0.46	0.61

[0159]

From the results shown in Table 3, it is apparent that the toners obtained by adding a long chain fatty acid or a salt thereof in the final stage can effectively control the liberation of the constituent external additives by the binding effect of the long chain fatty acid or a salt thereof. The electrical resistivities of such toners are also in a proper range. As shown in the column (iii) in Table 3, it is apparent that these toners show a uniform electrification property as compared with any comparative example.

[0160]

For example, it is known that the toners obtained by adding a long chain fatty acid or a salt thereof in the final stage of the multistage process of the present invention are low in the liberation rate of silica fine particles and titanium oxide fine particles, especially the liberation rate of titanium oxide fine particles as compared with the samples in Comparative Examples 1 to 3 and 5 and 6 wherein a long chain fatty acid or a salt thereof is not added. Further, these toners also show low liberation rate of silica fine particles and titanium oxide fine particles as compared with the samples in Comparative Examples 4 and 7 wherein a long chain fatty acid or a salt thereof is added by one time addition.

[0161]

From the comparison of the results in Examples 1 to 3 and the result in Comparative Example 3, it can be seen that the amounts of free silica fine particles and titanium oxide fine particles are reduced (in other words, silica fine particles are efficiently surrounded by toner mother particles) by adding the metal salt of long chain fatty acid (magnesium stearate) after the addition of positively electrifiable silica fine particles (Example 1), or by adding the metal salt of long chain fatty acid simultaneously with positively electrifiable silica fine particles (Examples 2 and 3). Accordingly, it becomes possible to reduce the fluctuation of electric charge at use time with the lapse of time.

[0162]

Of these toners, in particular the toners in Examples 2 and 3 are excellent in the uniformity of electrification, the liberation rate of silica fine particles and titanium oxide fine particles is low and excellent toners. Therefore, it is expected that a uniform electrification property will be maintained at use time.

[0163]

The samples obtained in Examples 2 and 3, 8 to 13 and Comparative Example 3 underwent the durability test. The results obtained are shown in Table 4 below.

[0164]

Table 4

		(i)		(ii)	(iii)	Electrical Resistivity ($\Omega \cdot \text{cm}$)	Liberation Rate of Silica (%)	Liberation Rate of Titanium Oxide (%)
		Q_1/m_1 ($\mu\text{C/g}$)	Q_2/m_2 ($\mu\text{C/g}$)					
Example 2	Initial stage	-11.53	-11.66	0.13		4.4×10^{16}	0.38	0.51
	After printing 3,000 sheets	-15.29	-17.81	2.52		5.3×10^{16}	0.42	0.69
Example 3	Initial stage	-11.56	-11.69	0.13		4.1×10^{16}	0.39	0.43
	After printing 3,000 sheets	-12.79	-13.56	0.77		4.3×10^{16}	0.38	0.63
Example 8	Initial stage	-11.22	-12.56	1.44		4.2×10^{16}	0.35	0.48
	After printing 3,000 sheets	-13.21	-14.69	1.48		5.1×10^{16}	0.38	0.52
Example 9	Initial stage	-12.69	-13.11	0.42		4.7×10^{16}	0.36	0.47
	After printing 3,000 sheets	-13.89	-14.51	0.62		4.7×10^{16}	0.41	0.42
Example 10	Initial stage	-13.52	-14.62	1.10		4.2×10^{16}	0.45	0.37
	After printing 3,000 sheets	-15.21	-16.35	1.14		4.2×10^{16}	0.44	0.48

		(i)	(ii)	(iii)	Electrical Resistivity ($\Omega \cdot \text{cm}$)	Liberation Rate of Silica (%)	Liberation Rate of Titanium Oxide (%)
		Q_1/m_1 ($\mu\text{C/g}$)	Q_2/m_2 ($\mu\text{C/g}$)	(i)-(ii) ($\mu\text{C/g}$)			
Example 11	Initial stage	-14.62	-15.88	1.26	4.2×10^{16}	0.48	0.44
	After printing 3,000 sheets	-14.61	-16.22	1.61	8.9×10^{16}	0.51	0.59
Example 12	Initial stage	-14.89	-16.21	1.32	4.2×10^{16}	0.37	0.46
	After printing 3,000 sheets	-15.97	-17.35	1.38	5.9×10^{16}	0.44	0.57
Example 13	Initial stage	-11.63	-13.51	1.88	4.2×10^{16}	0.51	0.48
	After printing 3,000 sheets	-13.02	-15.68	2.66	4.1×10^{16}	0.58	0.65
Comparative Example 3	Initial stage	-12.96	-16.31	3.35	4.5×10^{16}	0.46	1.28
	After printing 3,000 sheets	-14.81	-19.63	4.82	6.2×10^{16}	0.49	1.58

[0165]

As is apparent from the results in Table 4, in any example of the invention, the liberation rate of silica fine particles and titanium oxide fine particles is not so great as in the comparative example even after durability test as compared with the toner in Comparative Example 3. Further, the values in column (iii) in Table 4 which show the uniformity of electrification also do not so increase as the increase in the comparative example. That is, the uniformity of electrification is maintained better than that in the comparative example even when the number of sheets of printing increases. Thus, in the toners which are obtained by adding the salt of long chain fatty acid in the final stage of the multistage process, the liberation of the external additives from the toner mother particles is prevented by the binding effect of the long chain fatty acid or a salt thereof. As a result, extreme reduction of the electrical resistivity can be avoided and uniform electrification property can be maintained even after the number of sheets of printing has increased.

[0166]

To compare the toner in Example 2 and the toner in Example 3, these toners are both little in the liberation of titanium oxide fine particles after printing of 3,000 sheets and uniform electrification property is maintained,

but it can be understood that the increase in liberation rate is less in the toner obtained in Example 3 wherein negatively electrifiable silica fine particles a1 and a2 each having different particle size are used in combination than in the toner obtained in Example 2 wherein negatively electrifiable silica fine particles each having different particle size are not used. This fact shows that the fluctuations of the quantity of electrification and the electrical resistivity, and the liberation of silica and titanium oxide fine particles with the increase in the number of sheets of printing can be restrained by using two kinds of negatively electrifiable silica fine particles having different sizes respectively in an appropriate mass ratio.

[0167]

(EXAMPLES 14 TO 20 AND COMPARATIVE EXAMPLES 8 TO 10)

Each of the toners in Examples 14 to 20 and Comparative Examples 8 to 10 was obtained by adding external additives shown in Table 5 below each in the prescribed amount and prescribed order as shown in Table 5 to 100 mass parts of negatively electrifiable toner mother particles comprising a polyester resin as the binding resin. The process of external addition was performed by using Henschel Mixer FM20B (a product of MITSUI MINING COMPANY, LIMITED), and stirring the external additives for 3 minutes

with ZOSO type stirring blades, at 2,000 rpm. The process of external addition in each stage was performed on the same condition. The external additives used, the amounts and the addition order are shown in Table 5.

[0168]

Table 5

	External Additives				Order of External Addition			
	a1	b	c	d	First Stage	Second Stage	Third Stage	Fourth Stage
Example 14	-	1.0	1.0	0.2	c	b+d	-	-
Example 15	1.0	0.5	0.5	0.2	a1+c	b	d	-
Example 16	1.0	0.5	0.5	0.2	a1+b+c	d	-	-
Example 17	1.0	0.5	0.5	0.2	b	a1	c	d
Example 18	1.0	0.5	0.5	0.2	b	a1	c+d	-
Example 19	1.0	-	0.5	0.2	a1+c	d	-	-
Example 20	-	-	0.5	0.2	c	d	-	-
Comparative Example 8	-	1.0	-	0.2	c+d	-	-	-
Comparative Example 9	-	1.0	1.0	-	b+c	-	-	-
Comparative Example 10	-	1.0	1.0	0.2	b+d	c	-	-

The numeral in the column of External Additives shows the addition amount (mass parts) to 100 mass parts of toner mother particles.

[0169]

The toners obtained in Table 5 above were evaluated according to the evaluation methods described above. The results obtained are shown in Table 6 below.

[0170]

Table 6

	(i)	(ii)	(iii)	Electrical Resistivity ($\Omega\cdot\text{cm}$)	Liberation Rate of Silica (%)	Liberation Rate of Titanium Oxide (%)
	Q_1/m_1 ($\mu\text{C/g}$)	Q_2/m_2 ($\mu\text{C/g}$)	(i)-(ii) ($\mu\text{C/g}$)			
Example 14	-12.11	-14.53	2.42	4.3×10^{16}	0.35	0.52
Example 15	-15.21	-17.66	2.45	4.6×10^{16}	0.43	0.45
Example 16	-15.00	-16.72	1.72	4.3×10^{16}	0.41	0.43
Example 17	-16.23	-16.51	0.28	4.6×10^{16}	0.42	0.51
Example 18	-15.97	-16.24	0.27	4.1×10^{16}	0.45	0.47
Example 19	-16.02	-16.87	0.85	4.9×10^{16}	0.42	-
Example 20	-17.15	-17.46	0.31	4.6×10^{16}	0.51	-
Comparative Example 8	-14.66	-19.26	6.30	9.9×10^{16}	0.45	-
Comparative Example 9	-13.65	-19.68	6.03	5.6×10^{16}	0.46	0.89
Comparative Example 10	-9.25	-15.73	6.48	8.3×10^{16}	0.86	0.56

[0171]

From the results shown in Table 6, it is apparent that the toners obtained by adding a long chain fatty acid or a salt thereof in the final stage can effectively control the liberation of the constituent external additives by the binding effect of the long chain fatty acid or a salt thereof. The electrical resistivities of such toners are also in a proper range. As shown in the column (iii) in Table 6, it is apparent that these toners show a uniform electrification property as compared with any comparative example.

[0172]

For example, it is known that the toners obtained by adding a long chain fatty acid or a salt thereof in the final stage of the multistage process of the invention are low in the liberation rate of silica fine particles and titanium oxide fine particles, especially the liberation rate of titanium oxide fine particles as compared with the samples in Comparative Examples 8 and 9 which are not subjected to multistage process. Further, when Comparative Example 8, wherein a long chain fatty acid or a salt thereof is added by one time addition, and Example 20 are compared, it can be seen that the liberation rates of silica fine particles are not so greatly different, but the electrical resistivity of the toner in Example 20 is in a

proper range and excellent in the uniformity of electrification.

[0173]

The samples obtained in Examples 14 to 20 and Comparative Example 8 underwent the durability test. The results obtained are shown in Table 7 below.

[0174]

Table 7

		(i)	(ii)	(iii)	Electrical Resistivity ($\Omega\cdot\text{cm}$)	Liberation Rate of Silica (%)	Liberation Rate of Titanium Oxide (%)
		Q_1/m_1 ($\mu\text{C/g}$)	Q_2/m_2 ($\mu\text{C/g}$)	(i)-(ii) ($\mu\text{C/g}$)			
Example 14	Initial stage	-12.11	-14.53	2.42	4.3×10^{16}	0.35	0.52
	After printing 3,000 sheets	-13.34	-15.36	2.02	4.6×10^{16}	0.41	0.65
Example 15	Initial stage	-15.21	-17.66	2.45	4.6×10^{16}	0.43	0.45
	After printing 3,000 sheets	-16.66	-17.65	0.99	5.1×10^{16}	0.46	0.51
Example 16	Initial stage	-15.00	-16.72	1.72	4.3×10^{16}	0.41	0.43
	After printing 3,000 sheets	-16.10	-17.06	0.96	4.1×10^{16}	0.50	0.46
Example 17	Initial stage	-16.23	-16.51	0.28	4.6×10^{16}	0.42	0.51
	After printing 3,000 sheets	-17.35	-18.06	0.71	4.9×10^{16}	0.42	0.55
Example 18	Initial stage	-15.97	-16.24	0.27	4.1×10^{16}	0.45	0.47
	After printing 3,000 sheets	-17.05	-17.85	0.80	2.4×10^{16}	0.50	0.59

		(i)	(ii)	(iii)	Electrical Resistivity ($\Omega\cdot\text{cm}$)	Liberation Rate of Silica (%)	Liberation Rate of Titanium Oxide (%)
		Q_1/m_1 ($\mu\text{C/g}$)	Q_2/m_2 ($\mu\text{C/g}$)	(i)-(ii) ($\mu\text{C/g}$)			
Example 19	Initial stage	-16.02	-16.87	0.85	4.9×10^{16}	0.42	0.09
	After printing 3,000 sheets	-17.21	-17.49	0.28	5.3×10^{16}	0.44	0.10
Example 20	Initial stage	-17.15	-17.46	0.31	4.6×10^{16}	0.51	0.08
	After printing 3,000 sheets	-18.25	-18.69	0.44	4.2×10^{16}	0.59	0.09
Comparative Example 8	Initial stage	-13.65	-19.68	6.03	5.6×10^{16}	0.46	0.89
	After printing 3,000 sheets	-21.39	-30.65	9.26	4.9×10^{18}	0.88	0.91

[0175]

As is apparent from the results in Table 7, in any example of the invention, the liberation rate of silica fine particles and titanium oxide fine particles is not so great as in the comparative example even after durability test as compared with the toner in Comparative Example 8. Further, the values in column (iii) in Table 7 which show the uniformity of electrification also do not so increase as the increase in the comparative example. That is, the uniformity of electrification is maintained better than that in the comparative example even when the number of sheets of printing increases. Thus, in the toners which are obtained by adding the salt of long chain fatty acid in the final stage of the multistage process, the liberation of the external additives from the toner mother particles is prevented by the binding effect of the long chain fatty acid or a salt thereof. As a result, uniform electrification property can be maintained even after the number of sheets of printing has increased.

[0176]

[Effect of the Invention]

The toner in the present invention is obtained by adding a long chain fatty acid or a salt thereof in the final stage of the multistage process. It is thought that, by adding in the final stage, the long chain fatty acid or

a salt thereof functions as the binding agent of external additives, e.g., negatively electrifiable silica fine particles, positively electrifiable silica fine particles, and titanium oxide fine particles, and restrains the liberation of these external additives from the toner surface. It is also thought that the effect of the long chain fatty acid or a salt thereof as the lubricant of the toner is further exhibited and the uniformity of electrification is maintained by adding the long chain fatty acid or a salt thereof in the final stage. Further, the stability of electrification of the toner of the invention is maintained in repeating use. This is presumed to be the result that the long chain fatty acid or a salt thereof prevents the coagulation of the toner as the lubricant, and the external additives are prevented from being buried in toner mother particles due to the friction of toner particles. Further, it is thought that the toner is brought into contact with the photosensitive material in the developing chamber, thereby the long chain fatty acid or a salt thereof migrates to the surface of the photosensitive material and lubricates the surface of the photosensitive material, as a result, the photosensitive material is prevented from being abraded by the external additives on the surface of the toner.

[Designation of Document] ABSTRACT

[Abstract]

[Problem] To provide a toner which is low in desorption of silica fine particles or titanium oxide fine particles, which can maintain the electrification property for a long period of time, shows high flowability.

[Means for Solving the Problem] The present invention provide a toner comprising toner mother particles containing a binding resin and a colorant having added therinto external additives by multistage process, and particles comprising at least a long chain fatty acid or a salt thereof are added in the final stage of the multistage process. By adding external additives, e.g., negatively electrifiable silica fine particles, titanium oxide fine particles and positively electrifiable silica fine particles, by multistage process, the external additives are strongly adhered to the toner mother particles from the relationship of the work functions of these external additives and the toner mother particles, or from the relationship of the static attraction between the external additives and the toner mother particles, further, the liberation of the external additives from the toner mother particles is restrained by the binding function of the long chain fatty acid or a salt thereof added in the final stage,

so that an electrification property is maintained uniformly
for a long period of time.

[Representative Drawing] none